

# The Atmosphere as Laboratory: Aeronomy by Astronomy

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## Abstract

Astronomical sky spectra, which are byproducts of long-slit observations with echelle spectrographs on large telescopes, provide a unique platform for studying the optical emissions of excited molecules and atoms in the terrestrial atmosphere that can greatly extend present knowledge based on laboratory spectra. This paper summarizes some of the advances that have been made in our understanding of the lower electronic states of  $O_2$  and other species from the sky spectra and from direct observations of the Venus nightglow.

## 1. Introduction

Astronomical sky spectra are proving to be a rich source of information on emissions in the terrestrial atmosphere, over a broad range of altitudes (85-250 km). The high resolution (0.01 nm) and CCD detection associated with these spectra has led to a variety of new observations, on species as diverse as the electronically-excited states of  $O_2$ , many  $O$ -atom Rydberg levels,  $OH$ ,  $K$ ,  $N_2^+$ ,  $He$ , and  $Ca^+$ , over the 330-1000 nm spectral region. From nightglow emission, we have been able to characterize the  $O_2$  states in vibrational levels not previously observed, and have detected  $O_2(b)$  state emission from levels  $v = 0-15$ , emission to the  $O_2(a)$  state in levels  $v = 1-11$ , and emission to the ground state in levels  $v = 0-15$ . In addition, we are able to see the fully-resolved  $O_2$  UV emissions in the Herzberg I and Chamberlain transitions. There is considerable synergy when we observe the new atmospheric emissions while simultaneously studying the same emitters in the laboratory. [KTC00] In related astronomically-oriented work, we have also made measurements of the Venus nightglow with the Keck and APO telescopes, confirming older results which identified  $O_2(c)$  state emission, and establishing for the first time that the oxygen 557.7 nm green line is an important Venus nightglow feature. Examples of the terrestrial spectra are available at <http://www-mpl.sri.com/NVAO/download/Osterbrock.html>.

## 2. Discussion

A broad range of emission features are to be found in the sky spectra that we have obtained from the two echelle spectrometers on the Keck telescopes on Mauna Kea, HIRES on Keck I and ESI on Keck II. In general, the HIRES data have been taken at a resolution of 40,000, while the ESI resolution is 8000. For accurate spectroscopy, HIRES is far better, but ESI, having higher sensitivity, collects data more rapidly, and thus is more useful for temporal studies.

Figures 1-5 show examples of what can be obtained from sky spectra. In Figure 1 is shown a spectral region that has in the past been considered devoid of features, so much so that it has been used to measure the background continuum of the nightglow. The  $O_2(b-X)$  3-2 and 4-3 bands are in fact the strongest of the new  $b-X$  bands, so that choice was unfortunate. Figure 2 shows the range of  $b^1\Sigma_g^+$  state vibrational levels found in the nightglow. The structure of the distribution is not fully understood, but is caused by a combination of the production rates into these individual levels, and the collisional depopulation rates. These are now known

for a number of the levels for  $O_2$  and  $N_2$  colliders, but not yet for the potentially important  $O(^3P)$ . Table 2 shows the vibrational levels in both the  $b^1\Sigma_g^+$  and the  $a^1\Delta_g$  states that can be identified in the Keck spectra and from our current laboratory studies.

Table 1.  $O_2 (A^3\Sigma_u^+ - X^3\Sigma_g^-)$   
Bands Analyzed From Keck Sky Spectra (51 Bands).

height $v'/v''$	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
0					X	X	X	X	X						
1			X	X	X	X									
2	X	X	X	X	X			X	X						
3		X	X	X			X	X			X	X			
4		X	X			X	X			X	X			X	
5					X	X			X	X		X	X		
6				X	X			X	X		X				X
7				X	X		X	X		X	X			X	
8										X			X		

Table 2. Vibrational Levels Accessible in the Laboratory and in the Keck Sky Spectra for  $O_2(a^1\Delta_g)$  and  $O_2(b^1\Sigma_g^+)$ .

$a^1\Delta_g$ (Keck)	$v = 0-11$
$a^1\Delta_g$ (Lab)	$v = 0-2, 16-19$
$b^1\Sigma_g^+$ (Keck)	$v = 0-7, 9-15$
$b^1\Sigma_g^+$ (Lab)	$v = 0-3, 10-15$

Figure 3 shows that there are many bands in the blue spectral region, and these originate with the  $O_2$  Herzberg states,  $A^3\Sigma_u^+$ ,  $A'^3\Delta_u$ , and  $c^1\Sigma_u^-$ . Shown is the first atmospheric observation of resolved emission from the  $v = 0$  level of the  $A^3\Sigma_u^+$  state, which is interesting because of the implications about the development of the vibrational distribution of that state. The spectrum also shows the  $H_\beta$  line, which comes from the geocorona, far higher in the atmosphere than the  $O_2$  features; the next line in the Balmer series,  $H_\gamma$ , is also observed.

Figure 4 shows the presence of a previously unobserved system of  $O_2$ , the  $c$ - $b$  system. By comparison to the Herzberg I 3-9 band, one sees that it is not a weak transition, as the 3-9 band is one of the three strongest Herzberg I bands longward of 380 nm. The very open structure of the  $c$ - $b$  bands is a consequence of the fact that only a Q-branch is observed, and that only alternate rotational levels are populated. Radiative recombination, in which ions and electrons recombine, is a significant ionospheric process. The product is a Rydberg atom, in any of the states up to the  $O$ -atom ionization limit. The well-known examples of this process, from ground-based observations, are the 777.4 and 844.6 nm multiplets. However, there are many such multiplets, originating with higher energy levels. Figure 5 shows a particularly clear example, the  $5d$ - $3p$  set of lines in the quintet manifold. The quintets are more prominent in the atmosphere than the triplets, yet laboratory data on the quintets are sparser.

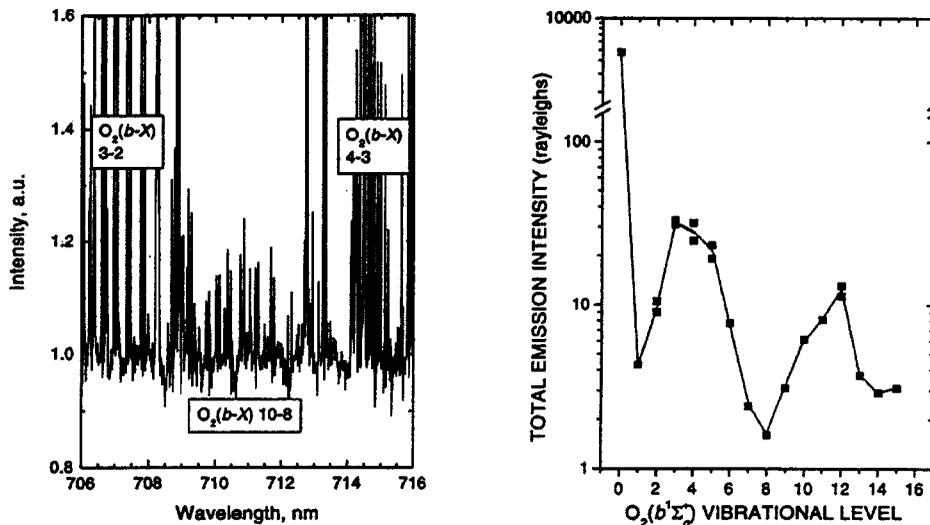


Fig. 1. (LEFT): Until the Keck spectra became available, the only rotationally-resolved atmospheric emission spectrum of the  $O_2$  Atmospheric band system was of the 0-1 band at 865 nm. We now have  $\sim 30$  resolved bands, of which a sample is shown. Bands are observed up to  $b^1\Sigma_g^+$  ( $v = 15$ ). Summing of files greatly improves the S/N ratio.

Fig. 2. (RIGHT): There are numerous  $O_2(b-X)$  bands seen in the nightglow. By making calibrations against nearby  $OH$  bands, we have calculated a vibrational distribution for the  $b^1\Sigma_g^+$  ( $v$ ) population. It is tri-modal, the low population near  $v = 1$  presumably related to rapid quenching, and the high population at  $v = 0$  originating from lack of quenching. The minimum at  $v = 8$  is not yet understood, while the increase at higher levels is probably related to cascading from Herzberg states.

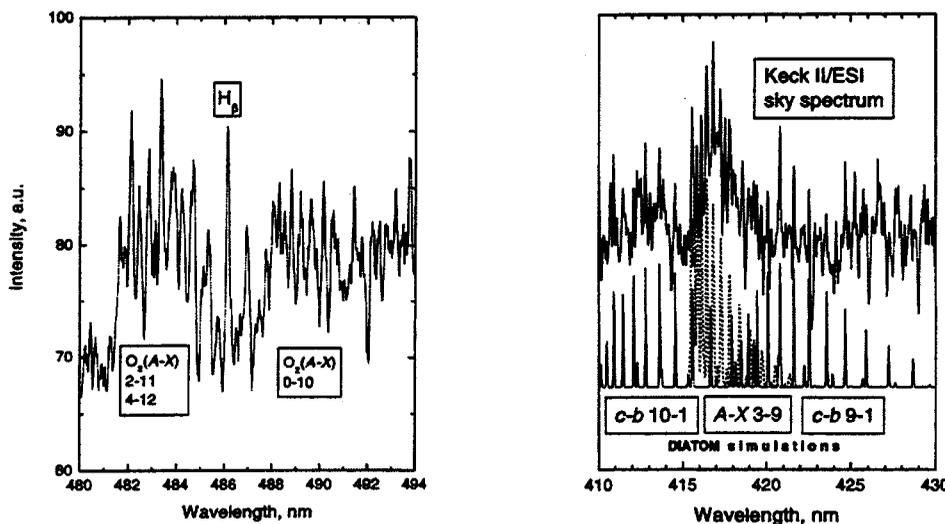


Fig. 3. (LEFT): The  $O_2$  Herzberg I bands are generally considered to be a UV system. The detector sensitivity seen in the Keck spectra permits measurements well into the visible. Shown is the first demonstration of atmospheric emission from the  $v = 0$  level of the  $A^3\Sigma_u^+$  state, which is significant because it involves collisional cascading at very low densities, 1 mTorr and less. Table 1 shows the range of  $emph{A-X}$  bands that have been analyzed in the Keck spectra, which are considerably improving our knowledge of  $O_2$  ground state spectroscopy. Similarly, the many Chamberlain ( $A'-a$ ) bands that appear supply information on the  $a^1\Delta_g$  state.

Fig. 4. (RIGHT): The  $O_2(c^1\Sigma_u^- - X^3\Sigma_g^-)$  Herzberg II system has been considered as the only significant emission from the  $O_2(c)$  state, and its emission is very strong in the atmosphere of Venus. Shown in this figure is a new optical transition, the  $c^1\Sigma_u^- - b^1\Sigma_g^+$  system. In the terrestrial nightglow, where the  $O_2(c-X)$  emission is weak, it turns out that the  $c-b$  bands are much easier to observe, due to the details of the relevant spectroscopy.

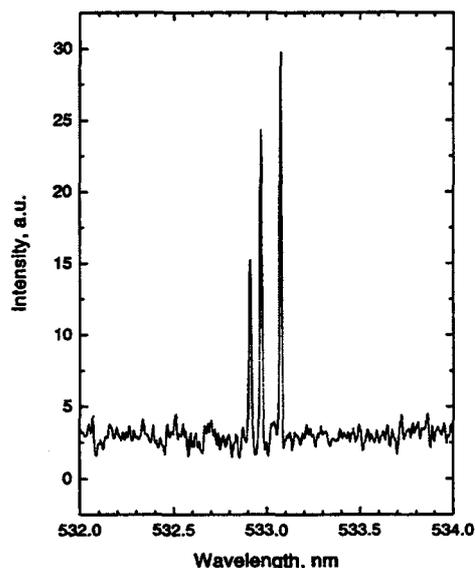


Fig. 5. Ionospheric emission at 777.4 and 844.6 nm is a measure of various processes, but in the nightglow these emissions arise from radiative recombination of  $O^+$ . This interaction produces a variety of other transitions not normally seen in the atmosphere, and never previously reported in the nightglow. Shown is the triplet of lines of the  $5d-3p$  transition of the quintet  $OI$  manifold, one multiplet of some thirty that have been identified in the Keck spectra. Observation of these lines is free of the  $OH$  contamination existing in other spectral regions.

### 3. Conclusions

Sky spectra provide a window into the atmosphere that has not previously been exploited. Previous optical aeronomic studies focused on the strongest emitters, regardless of whether the chemistry of other species might be important. We are now able to observe a much larger range of species, which simultaneously gives a stimulus to observing these entities in the laboratory. A good example is the range of vibrationally excited levels in the  $O_2(b\ ^1\Sigma_g^+)$  state, which after their initial detection in the Keck sky spectra were found in laboratory experiments to be generated from collisional relaxation of the Herzberg states. At the same time, the analogous interaction was found for the  $O_2(a\ ^1\Delta_g)$  state. These relaxation pathways were not previously known. The precision of the astronomers' wavelength calibration has enabled us to make spectroscopic advances, particularly for the lowest three  $O_2$  states. Long-standing discrepancies in the ground state levels have been corrected, the  $a\ ^1\Delta_g$  state levels are now known over a much wider range, as is also true for the  $b\ ^1\Sigma_g^+$  state. The discovery of the  $O_2(c-b)$  bands will lead to improved rotational constants for both states, and also provides a means of monitoring the  $c\ ^1\Sigma_u^-$  state in the terrestrial atmosphere, an ability that was previously marginal at best. The range of ionospheric emissions detectable from the ground has been expanded. Not only can one see a large variety of  $O^+$  transitions, but the rotational distribution in the  $O_2(b-X)$  1-1 band, generated by  $O(^1D) + O_2$  energy transfer, provides a method of measuring thermospheric temperatures. Given that sky spectra are being generated world-wide at all major observatories, aeronomers have new opportunities to make advances in the field.

### Acknowledgments

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### REFERENCES

Kalogerakis, K. S., Totth, A., Cosby, P. C., Slanger, T. G., and Copeland, R. A. 2000, *Eos, Trans. Amer. Geophys. Union*, **81**, F944.

Also see the paper in these proceedings by Kalogerakis *et al.* *Research on Electronically- and Vibrationally-Excited O<sub>2</sub>, with Application to Planetary and Terrestrial Atmospheres.*